Patented May 12, 1931 1,804,451

# UNITED STATES PATENT OFFICE

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## PROCESS OF TREATING PETROLEUM

No Drawing. Application filed June 6, 1925. Serial No. 35,476.

This invention relates to the treatment of petroleum and comprises a process whereby saponifiable constituents are extracted and recovered from distillation residues obtained during the refining of petroleum oils.

The invention contemplates the recovery of saponifiable constituents from residues derived from the distillation of petroleum oils in the presence of alkaline material, by extracting the alkali salts from the residues of the said distillation by means of alcohol.

Certain crude petroleums, particularly the nonparaffin base crudes obtained in the Gulf coastal fields of the United States, contain appreciable quantities of saponifiable constituents which are of such nature as to be valuable in the manufacture of soaps, greases and like products for which animal and vegetable oils are ordinarily used. The crude oils of this type are usually comparatively heavy oils containing only a small quantity of the lighter hydrocarbons such as gasoline or naphtha. However, upon distillation, these crudes yield large quantities of fractions suitable as raw stock for the manufacture of high grade lubricating oils, as much as 30 to 40 percent of the crude usually being suitable for this purpose.

In the refining of crude oils of this type for the manufacture of lubricating oils, the first step consists in a distillation in which the oil is roughly separated into three major portions consisting of a lighter portion such as gas oil, an intermediate portion which is the lubricating oil distillate, and the heavy tarry still residues. The intermediate portion is further refined by treatment with sulfuric acid, filtration and the like to yield stable products of merchantable grade.

It has been found that the lubricating oil fraction from such petroleums may contain considerable quantities of saponifiable constituents which may range from one-half to three percent by weight of the oil, and that these compounds, if present in the oil during the subsequent acid treating, will frequently cause difficulty by the formation of refractory emulsions. A preferred method of removing these saponifiable compounds from the oil is to conduct the distillation in the presence of an alkaline material. The alkali may be supplied during the distillation of the crude oil or the lubricating oil fraction may be redistilled in the presence of alkaline material, but in either case, the resulting lubricating oil fraction after such treatment is practically free from saponifiable constituents and is in proper condition for refining with acid.

As a result of the reaction between the saponifiable constituents and the alkaline material during distillation, alkali salts are formed which are comparatively non-volatile and which are thereby concentrated in the distillation residues, and it is a particular object of this invention to concentrate the saponifiable constituents of petroleum by subjecting the oil to distillation in the presence of alkaline material, thus aiding in the subsequent recovery of these constituents.

Now we have found that by treating the residues resulting from the distillation of petroleum in the presence of alkaline material with alcohol, the alkali salts which are formed during the distillation by the reaction between the saponifiable constituents and the alkaline materials are dissolved and may thus be separated from the heavy hydrocarbon portion of the residue which is relatively insoluble in alcohol.

In the practice of the invention a preferable procedure is as follows:

The distillation residue or still bottoms resulting from the distillation of petroleum in the presence of alkaline material, such for example as caustic soda, is treated with alcohol in any suitable container or vessel. The residue may constitute from 2 to 25 percent by volume of the original crude oil and may contain up to from 30 to 40 percent of the alkali salts of the saponifiable material. The treatment with alcohol is more effective when carried out under the influence of heat and is best carried out in a closed vessel fitted with steam coils or jacket for heating and supplied with a reflux condenser to prevent loss of alcohol from volatilization. Means for agitating and stirring the contents of the vessel will aid materially in reducing the time required in the extraction process.

After thoroughly stirring the still bottoms and alcohol while under the influence of heat, the mixture is allowed to cool somewhat and to separate into two layers, the upper layer consisting of the alkali salts in alcoholic solution while the lower layer consists of the heavy hydrocarbon oil portion, of the still residue. During the period of settling, boiling of the alcohol is to be avoided as this would result in the prevention of a clean separation of the oil and alcohol layers. After the separation of the two layers is substantially complete the alcohol layer is drawn off and may then be subjected to distillation for the removal of the alcohol from the alkali salts dissolved therein. The alcohol thus recovered may be used again in extracting a fresh portion of the distillation residue. The hydrocarbon portion of the distillation residue may be used as a fuel either alone or in mixture with lighter oils or for any other suitable purpose.

The alcohol used in the extraction of the alkali salts may vary in purity and may contain some water and, although the best results have been obtained from the use of 95% ethyl alcohol, satisfactory extraction may be accomplished with as low as 80% solutions of ethyl alcohol in water. The usual denaturants contained in denatured ethyl alcohol do not affect its extraction properties to an appreciable degree and in general denatured ethyl alcohol is a satisfactory solvent for this purpose. However, ethyl alcohol is not the only alcohol suitable for extracting the alkaline salts of saponifiable constituents of petroleum, and methyl, isopropyl, or other of the lower molecular weight aliphatic alcohols may be satisfactorily used in the process, although it is preferable to use the cheapest solvent which will accomplish the desired separation.

In order that the invention may be more fully understood, the following specific example of the operation of the process will be described.

A typical crude petroleum from the Gulf coastal fields is distilled by the aid of heat and steam in the usual manner, yielding approximately 35 percent by volume of a fraction suitable for the manufacture of lubricating oil. This fraction is then redistilled in the presence of caustic soda, using a slight excess of caustic over and above that required for complete reaction with the saponifiable constituents of the oil, and the distillation is continued until about 5 percent of the lubricating fraction remains in the still. This distillation residue while hot enough to remain in a fluid condition, is drawn into the extraction vessel and is then treated with approximately its own weight of 95% ethyl alcohol, the mixture being thoroughly stirred while the temperature is maintained at about 170° F. After stirring for one hour, the mixture is allowed to settle for three hours during which time stratification of the oil and alcohol layers takes place. The alcohol layer is then withdrawn from the vessel and the alcohol is distilled from the dissolved sodium salts, yielding approximately 30 percent by weight of the crude salts of the saponifiable material from the distillation residue. The sodium salts thus obtained will usually contain traces of hydrocarbon oil, but may be used in the crude form as soap stock or in the manufacture of greases or they may first be subjected to further purification by any suitable means.

Although the above described example refers to the recovery of saponifiable constituents from the alkali distillation residue of an unrefined distillate oil, the process is equally adapted for the recovery of similar constituents from the alkali distillation residues from any petroleum oil which may contain saponifiable constituents.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore, only such limitation should be imposed as are indicated in the appended claims.

We claim:

1. A method of treating naphthenic base crude petroleums for the recovery of naphthenic acids therefrom, which comprises, separating the crude oil by distillation into three major portions, consisting essentially of a light oil distillate, an intermediate lubricating oil distillate containing a substantial quantity of naphthenic acids and a heavy still residue, redistilling the lubricating oil distillate in the presence of alkali to produce redistilled lubricating oils substantially free from naphthenic acids and a small still residue containing in concentrated condition the alkali salts of the naphthenic acid content of the original lubricating oil distillate, treating this still residue with alcohol to dissolve the alkali salts, and separating the alcoholic solution of the alkali salts from the residual hydrocarbon oil.

2. A method of treating naphthenic base crude petroleums for the recovery of naphthenic acids therefrom which comprises, distilling from the crude petroleum a lubricating oil distillate consisting of thirty to forty per cent of the crude oil and containing a substantial quantity of naphthenic acids, redistilling the major portion of the lubricating oil distillate in the presence of alkali to produce redistilled lubricating oils substantially free from naphthenic acids and a small still residue containing in concentrated condition the alkali salts of the naphthenic acid content of the original lubricating oil distillate, treating this still residue with eighty to ninety per cent ethyl alcohol, and separat-

ing the alcoholic solution of the alkali salts from the residual hydrocarbon oil.

3. A method of treating naphthenic base crude petroleums for the recovery of naphthenic acids therefrom which comprises, separating by distillation from the crude petroleum a fraction for the manufacture of lubricating oil containing a substantial quantity of naphthenic acids, redistilling said fraction in the presence of caustic soda to produce redistilled lubricating oils substantially free from naphthenic acids and a small still residue said residue having approximately five per cent of the volume of said fraction, treating this undistilled residue with alcohol to dissolve the alkali salts, and separating the alcoholic solution of the alkali salts from the residual hydrocarbon oil.

In witness whereof we have hereunto set our hands this 27th day of May, 1925.

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